Theoretical Studies of Actinide Complexes in Solution Using Density Functional Theory

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Los Alamos has been long been recognized as one of the world's leading centers for its capabilities in experimental studies of actinide chemistry, particularly of the transuranic elements. In collaboration with our experimental colleagues in Nuclear Materials Technology (NMT) and Chemical Science and Technology (CST) Divisions, we have had the opportunity in recent years to develop theoretical capabilities to study the properties of actinide molecules in solution.

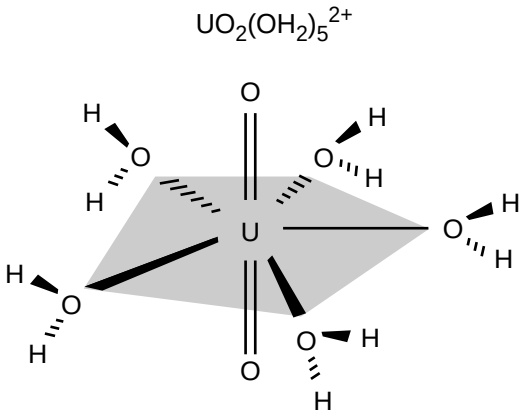

Figure 1: Schematic geometrical structure of $UO_2(H_2O)_5^{2+}$.

Obtaining an accurate description of the electronic structure and solution properties of actinide species is a significant challenge to the theorist. Relativistic effects play an important role in the chemistry of molecules containing heavy atoms such as uranium or plutonium. The fact that electron-electron electrostatic interactions, spin-orbit coupling, and electron correlation effects are all of the same magnitude presents difficulties for theoretical approaches.

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We have been examining the structures and properties of actinide complexes using density functional theory and relativistic effective core potentials. The chemistry of actinides is characterized by a variety of oxidation states and coordination numbers. An important class of such complexes are actinyl species AnO_2^{2+} and AnO_2^{+} containing the linear O=An=O species (where An = U, Np, Pu) for the +6 and +5 oxidation states, respectively, with other ligands such as water coordinated in the equatorial plane (Figure 1). We have systematically examined the structures and vibrational properties of the aquo species $UO_2(H_2O)_5^{2+}$ and the Np and Pu counterparts and the corresponding reduced species such as $UO_2(H_2O)_5^{+}$. The geometry of each complex is fully optimized using the "hybrid" B3LYP density functional, and the frequencies are computed using analytic second derivatives of the potential energy surface.

The theoretical results can be compared to experimental Raman spectroscopic studies of these species in solution, where the "Raman-active" symmetric stretch mode of the AnO_2 unit can be excited. The calculated and experimental results are compared in Figure 2 for both families of complexes, where the stretching mode (ν_s) monotonically decreases in the calculations as one goes down the actinide series U (908 cm^{-1}) to Np (854 cm^{-1}) to Pu (805 (cm^{-1}), as is also observed experimentally. The calculated and experimental results for the "infrared active" asymmetric mode (ν_{as}) are also shown. Interestingly, the actinyl bond lengths decrease slightly across the series U (1.756 Å calc., 1.76 Å expt.), Np (1.752 Å calc., 1.75 Å expt.), Pu (1.742 Å calc, 1.74 Å expt), as the vibrational frequency is also decreasing. The analysis of the wavefunctions attributes the decreasing bond strength to the decreasing overlap of the oxygen orbitals with the progressively smaller 5f orbital across the series.

In order to treat the solvent effects of the water molecules not bound in the first coordination shell, we use a dielectric continuum model developed at Los Alamos. In this model the dielectric response of the medium is obtained by solving Poisson's equation on a 3-dimensional surface surrounding the $UO_2(H_2O)_5^{2+}$ unit. Using this approach one obtains the free energy of solvation of the molecular species. We have examined several prototypical reactions in solution using the combination of hybrid density functional theory and the dielectric continuum solvent model. We have examined why the preferred configuration for the uranyl species in solution involves five water molecules and why the experimental redox potentials of the An(+6)/An(+5) couple—U (+0.06 eV), Np (+1.14 eV) and Pu (+0.91 eV)—vary in this manner across the series.

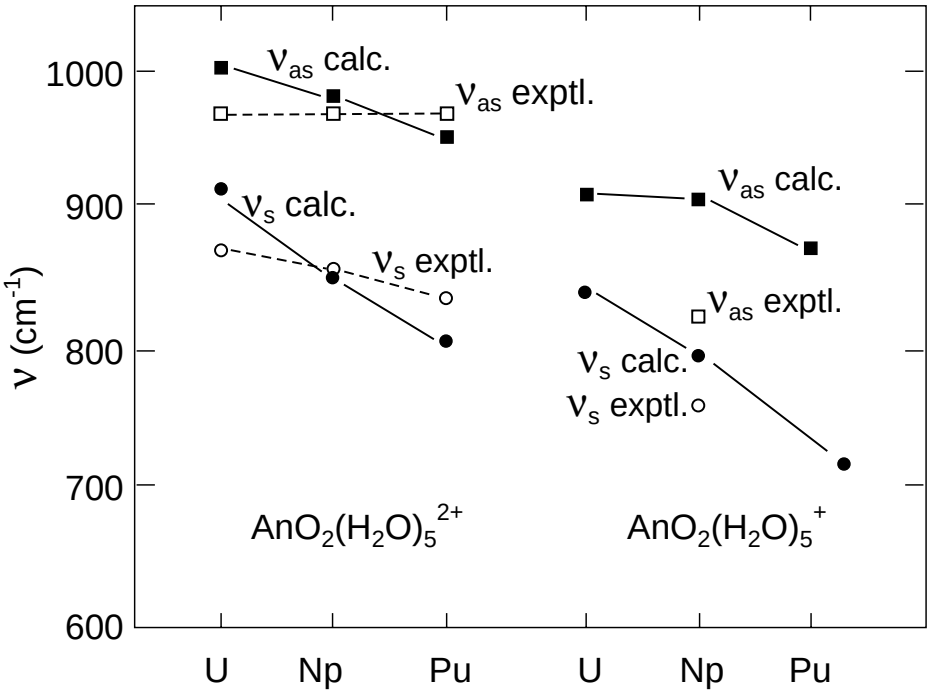

Figure 2: Comparison of calculated symmetric stretch (ν_s) and asymmetric stretch (ν_{as}) modes of the O=An=O unit in $AnO_2(H_2O)_5^{q+}$ complexes with experimental Raman and infrared measurements.